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# Study of Anion-Molecule Reaction Dynamics with Time-Dependent Photoelectron Spectroscopy

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A novel femtosecond time-resolved experiment has been set up to probe the photodissociation dynamics of negative ions and negative ion clusters. First results for the photodissociation of  $I_2^-$  have been obtained recently.

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## FINAL TECHNICAL REPORT

**TITLE:** Study of Anion-Molecule Reaction Dynamics with Time-Dependent Photoelectron Spectroscopy

**PRINCIPAL INVESTIGATOR:** Daniel M. Neumark

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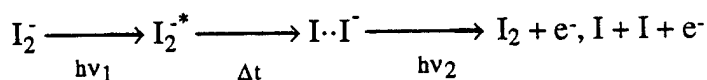
### Abstract:

A novel femtosecond time-resolved experiment has been set up to probe the photodissociation dynamics of negative ions and negative ion clusters. First results for the photodissociation of  $I_2^-$  have been obtained recently.

### Final Technical Report:

DURIP funds were used to purchase a Ti:sapphire femtosecond laser system (Model #CPA-1000 MPS) from Clark MRX Inc., at a cost of \$165,600. The Ti:sapphire femtosecond laser system is being used on a new experiment designed to study the photodissociation dynamics of negative ions and negative ion clusters on a femtosecond time scale. The novel feature of this experiment is that photoelectron spectroscopy is used to probe the dynamics of the dissociating anion in real-time. We have very recently obtained our first results on  $I_2^-$  photodissociation.

The principle of the experiment can be best understood by specifically considering its application to  $I_2^-$ :



This is a pump-probe experiment using two femtosecond laser pulses. The pump pulse ( $h\nu_1$ , 780 nm) excites mass-selected  $I_2^-$  from the ground  $X^2\Sigma_u^+$  state to the repulsive  $2\Pi_{u(3/2)}$  state. The  $I_2^-$  begins to dissociate, and after a variable time delay  $\Delta t$ , the dissociating ions are photodetached with the probe pulse ( $h\nu_2$ , 260 nm). We then measure the photoelectron spectrum, thereby mapping out the dissociating wave packet onto the well-known  $I_2$  potential energy surfaces.

At short times, one expects to see a transient associated with the dissociating  $I_2^-$  molecule, and at longer times, the  $I^-$  photoelectron spectrum should become more prominent as dissociation occurs. This is precisely what has been observed in our first measurements on  $I_2^-$ . However, the time scale for dissociation appears to be several hundred fsec longer than predicted by our simulations that use the currently accepted potential energy curves for  $I_2^-$ , indicating that these potentials may require significant modification. This issue will be addressed in further experiments and theoretical work.